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SURFACE TREATMENTS FOR PRECIPITATION -
HARDENING STAINLESS STEELS

By

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ABSTRACT

In this report, selected surface treatments that are applied to precipitation-hardenable stainless steels are discussed. The treatments covered are hard surfacing, electroplating, electroless plating, carburizing and decarburizing, nitriding, burnishing and other finishing operations, explosive hardening, planishing, and peening. Each treatment is described and its application to the precipitation-hardenable stainless steels is discussed. Reasons for using the treatments are discussed, problem areas are identified, and recommendations for research are made.

FOREWORD

Precipitation-hardening stainless steels are potentially useful wherever corrosion resistance and high strength at high temperatures are needed. They were developed initially to meet urgent requirements in World War II, but new alloys and methods of processing have since been introduced to assist engineers concerned with missiles and space vehicles and with various applications in the field of nuclear science and technology.

The Atomic Energy Commission and National Aeronautics and Space Administration have established a cooperative program to make available information, describing the technology resulting from their research and development efforts, which may have commercial application in American industry. This publication is one of the many resulting from the cooperative effort of these agencies to transfer technology to private industry.

This survey is based on information contained in a series of reports originally prepared by Battelle Memorial Institute for the Manufacturing Engineering Laboratory of the George C. Marshall Space Flight Center. The original information has been updated and revised in writing the current, seven volume survey. These volumes were prepared under a contract with the NASA Office of Technology Utilization which was monitored by the Redstone Scientific Information Center.

PREFACE

This report is one of a series of state-of-the-art reports prepared by Battelle Memorial Institute, Columbus, Ohio, under Contract No. DA-01-021-AMC-11651(Z), in the general field of materials fabrication.

The published information used in preparing this report was obtained from technical articles, reports on Government-sponsored research programs, and manufacturer's brochures. In locating this material, the following information centers, libraries, and abstract services were searched for the period from 1962 to the present:

Redstone Scientific Information Center
Defense Documentation Center
Defense Metals Information Center
The Libraries of Battelle
ASM Review of Metal Literature.

To obtain additional information and to ensure that the published information used in this report is up to date, personal contacts were made, by telephone or visit, with 20 individuals from 18 organizations. The individuals and companies are listed in the Appendix. The information cutoff date for this report was September 1, 1966.

The author wishes to thank each of these individuals and their organizations for their contributions. He also wishes to thank Vernon W. Ellzey and John A. Gibson, Battelle Project Technical Coordinators, and William L. Buckel and Mrs. Anita L. Coles, Battelle Information Specialists, for their assistance during the progress of this program.

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SURFACE TREATMENTS FOR PRECIPITATION - HARDENING STAINLESS STEELS

SUMMARY

The three types of precipitation-hardenable stainless steels that are available today offer a variety of effective combinations of corrosion resistance, strength, toughness, formability, weldability, and simplicity of heat treatment. The martensitic type offers moderate corrosion resistance and high strength resulting from a simple heat treatment. The semiaustenitic steels offer formability, weldability, high strength, and corrosion resistance. The austenitic precipitation-hardenable stainless steels retain high strength at elevated temperatures in addition to possessing a high degree of corrosion resistance and superior strength at ambient temperatures. These steels are strengthened by means of a single heat treatment.

In most applications for which these steels are chosen, it is their inherent properties that dictate their selection. The usual function of any surface preparation is to insure that these properties are operative.

However, there are instances in which special surface treatments are, or can be, applied to advantage. Usually, the surface treatment is designed to supply a property or characteristic that the steel does not, in itself, possess to the required degree but is vital to the particular application. Then, when this property is added, the material becomes an outstandingly good choice for the application. Conversely, there are surface treatments and surface conditions that are to be avoided in the precipitation-hardenable stainless steels. Examples of both are brought under discussion in this report.

Coating Treatments

On rare occasions, the martensitic and the austenitic precipitation-hardenable stainless steels are called on to serve in applications requiring a high degree of wear resistance in addition to their normal properties of corrosion resistance and strength. In these cases, the critical surfaces may be

coated with a hard facing alloy. The procedures used to hard face the martensitic types are designed to minimize the cracking that inevitably occurs when such coatings are applied to steels that undergo the austenite-to-martensite transformation on cooling from hardfacing temperatures. This transformation is accompanied by an expansion of the metal that is too great for the presently available brittle hard-surfacing alloys to negotiate.

Occasionally, some of the precipitation-hardenable stainless steels are electroplated. Those that contain appreciable amounts of titanium or aluminum may be electroplated with nickel or iron to facilitate brazing; these elements do not form oxide films that interfere with adhesion in the hydrogen brazing atmosphere as titanium and aluminum do. Again, these steels sometimes have been given a nickel-cadmium coating by electroplating, or a nickel-phosphorus coating by electroless plating, to increase their resistance to stress-corrosion cracking.

Carburizing is a surface treatment that is generally avoided in the precipitation-hardenable stainless steels. By tying up chromium in the form of chromium carbides and thus interfering with this element's capability to provide protection against corrosion, carburizing is detrimental to the steel's corrosion resistance. Also, it has an embrittling tendency, especially with the semiaustenitic and austenitic types. In addition, with the semiaustenitic steels, carburizing tends to unbalance the composition of the surface layers to the point that they may not martensitize, and harden, on cooling from elevated temperatures. On the other hand, the martensitic types are occasionally carburized to enhance resistance to wear and galling.

Scaling and decarburization usually are not problems with these steels. In fact, the precipitation-hardenable stainless steels are normally heat treated in an air atmosphere. However, when no oxidation or decarburization can be tolerated, heat treating must be carried out in pure, dry argon or hydrogen, or in a vacuum. When a thin scale can be tolerated, but the amount of scaling that takes place on heating in air is unacceptable, special protective coatings can be applied before heat treating in air. These coatings, usually proprietary, are designed to minimize scaling and to make subsequent scale removal by chemical means easier.

Nitriding is a different matter. All three types of precipitation-hardenable stainless steel have been nitrided. Although nitriding detracts from corrosion resistance in much the same manner as does carburizing, the process is nevertheless used to develop high surface hardness, increase wear resistance, develop antigalling properties, and improve fatigue resistance.

Heat-resistant diffusion coatings are not known to be applied to the precipitation-hardenable stainless steels. In general, these steels are not used at temperatures where such coatings would be an asset. The upper service temperatures for these steels are limited by their age-hardening temperatures which are usually quite moderate. When heated above their aging temperature range, these steels rapidly lose strength. For high-temperature applications, the standard nonage-hardening stainless steels are preferred.

Mechanical Treatments

No great amount of use is made of mechanical surface treatments such as burnishing, explosive hardening, planishing, or peening in the manufacture of components from the precipitation-hardenable stainless steels. However, on occasion such treatments are used, or can be used, to considerable advantage.

Burnishing is an effective means of improving the surface finish of small-to-medium sized articles. In the same equipment, i. e. , rotating barrels or vibrating tubs, certain additional important operations can be carried out in conjunction with, or in sequence with, burnishing. Such operations include cleaning the work, removal of scale, removal of slag remaining from thermal cutting operations, deburring, and the development of radii on the corners and edges of articles.

Some experimental work has been done on the explosive hardening of the austenitic type of precipitation-hardenable stainless steel, and interesting results have been obtained. Higher hardness values have been observed in explosively hardened and aged material than in material that received only the aging treatment. However, as yet, no industrial use of the process as a method of hardening precipitation-hardenable stainless steels has emerged. In fact, it is doubtful that the process is of much value with the harder, stronger martensitic and semiaustenitic alloys.

On the other hand, some experience has been acquired with the roll planishing of the semiaustenitic precipitation-hardenable type of stainless steel. This process has been used to contour butt-welded joints in thin sheet as well as to improve the mechanical properties of such joints.

The final mechanical treatment covered in this study is peening. The present-day industrial importance of this process stems from its capability to develop residual compressive stresses at the surface of the metal. Because of this capability peening serves numerous purposes. It is used to improve fatigue resistance, to correct distortion in welded and in unwelded components, to prevent cracking in welds, to improve resistance to stress-corrosion cracking, to form parts from light-gage sheet metal, and to promote recrystallization in welds and weld-heat-affected zones when annealed subsequent to the peening operation. Instances of the peening of precipitation-hardenable stainless steels are rare, but the capability of the process to improve the fatigue resistance of the austenitic type of precipitation-hardenable stainless steel has been demonstrated experimentally.

INTRODUCTION

There are three types of precipitation-hardenable stainless steel in existence today, martensitic, semiaustenitic, and austenitic. These types are distinguished from each other by the microstructures they develop on cooling from austenitizing, or solution annealing, temperatures.

In the martensitic types, the austenite that forms at elevated temperatures transforms to martensite on cooling to room temperature. This transformation results in an increase in strength and hardness. A further increment in hardness and strength occurs when the steel is reheated to intermediate temperatures at which it age hardens. The martensitic precipitation-hardenable stainless steels offer a combination of moderate corrosion resistance and high strength developed by a single heat treatment carried out at a moderate temperature. Examples of applications include brackets, clamps, rivets, and bolts for aircraft; valves and impellers for pumps; propeller shafting for boats; aircraft engine mounts; and components of papermaking machinery [1]. These steels are commonly used at yield strengths of 150 000 to 200 000 lb/in.² ($10\,341 \times 10^5$ to $13\,788 \times 10^5$ N/m²) the elongation values being in the range of 20 to 10 percent in 2 in. (5.08 cm) [2].

The semiaustenitic precipitation-hardenable stainless steels remain austenitic on cooling to room temperature from the temperatures at which they are solution annealed, generally, 1900° to 2000° F (1298° to 1353° K). In this condition, these alloys are readily cold formed and welded. Hardening involves converting the austenite to martensite and then aging at temperatures usually

in the range of 900° to 1050° F (748° to 831° K), resulting in a considerable increase in strength. The transformation of austenite to martensite can be brought about by cold working or by the precipitation of chromium carbides on reheating in the range of 1200° to 1750° F (913° to 1215° K). The depletion of the matrix in chromium and carbon that occurs raises the M_s temperature so that, on cooling to room temperature or to a convenient cryogenic temperature, the martensite transformation takes place. These steels are used at yield strengths ranging from 150 000 to 280 000 lb/in² ($10\,341 \times 10^5$ to $193\,032 \times 10^4$ N/m²), the corresponding elongations being about 12 to 2 percent in 2 in. (5.08 cm) [2].

The semiaustenitic stainless steels derive their name, then, from the fact that they are austenitic as annealed but, by appropriate treatment, can be made martensitic and age hardenable. Thus, these steels offer an excellent combination of corrosion resistance, formability, weldability, and high strength. Illustrative applications for these steels include stiffeners, interior frames, bulkheads, and longerons for aircraft; honeycomb sandwich structures for spacecraft and airframes; tanks, ducts, and skin for aircraft; boat shafts; saw blades; nuclear reactor components; and compressor discs [1].

The austenitic types do not transform on cooling from solution annealing temperatures or any other elevated temperature; they remain austenitic. These steels are strengthened by aging at appropriate intermediate temperatures following solution annealing. The austenitic age-hardenable stainless steels offer corrosion resistance, moderate strength at room temperature, and superior strength at elevated temperatures up to some 1300° F (968° K). A commonly used room-temperature yield strength is 100 000 lb/in² (6894×10^5 N/m²) with an elongation of 25 percent in 2 in. (5.08 cm); at 1200° F (913° K) a yield strength of some 88 000 lb/in² ($606\,672 \times 10^3$ N/m²) can be obtained [3]. Applications include jet engine turbine wheels and blades; casings, frames and other jet engine components; afterburner and tail cone parts; bolting and miscellaneous hardware; and aircraft arresting gear hook points [3,4].

The compositions of a number of precipitation-hardenable stainless steels are given in Table I [2]. Also included in the table are the forms in which the steels are available and the name of the concern where each alloy was originated. The physical metallurgy of the precipitation-hardenable stainless steels is quite complicated. As a consequence, these steels can be given a wide variety of thermal and mechanical treatments which result in an equally wide variety of mechanical properties. For further information on these subjects, attention is called to C. J. Slunder, A. F. Hoenie, and A. M. Hall [2].

TABLE I. PRECIPITATION-HARDENABLE STAINLESS STEELS

Alloy Type and Designation	Originator	Forms (a)	Chemical Composition, percent (b)											
			C	Cr	Ni	Cu	Al	Ti	Mo	Co	Cb-Ta	Si	Mn	Other
Martensitic	Armco Steel Corp.	B, F, C, S, P, W	0.07 Max	15.5-17.5	3-5	3-5						0.15-0.15	1 Max	1 Max
	Armco Steel Corp.	B, F, W	0.07 Max	14.0-15.5	3.3-5.5	2.5-4.5						0.15-0.15	1 Max	1 Max
	Armco Steel Corp.	B, F, P, W	0.06 Max	12.0-13.5	7-9		0.80-1.20		1.75-2.50			0.50 Max	0.50 Max	
	Allegheny-Ludlum Steel Co.	S, P	0.03	14.5	6-5			0.80				0.20	0.30	
	Allegheny-Ludlum Steel Co.	B, F, S, P	0.04	11.5	4-25			0.50				0.15	0.20	
	Carpenter Steel Co.	B, F, S, P	0.03 Max	11-13	7-10	1-3		0.90-1.40			0.25-0.50	0.50 Max	0.50 Max	B, 0.005 Max V, 0.5
	Crucible Steel Corp.	B, F, S, P	0.15	14.5					5	13.5				
Semiaustenitic	Armco Steel Corp.	S, P, B, W	0.09 Max	16-18	6.50-7.75								1 Max	1 Max
	Armco Steel Corp.	S, P, W, T, E	0.09 Max	14-16	6.30-7.75		0.75-1.50		2-3			1 Max	1 Max	1 Max
	Armco Steel Corp.	S, P	0.05 Max	13.0-15.5	7.5-9.5		0.75-1.50		2-3			1 Max	1 Max	1 Max
	Allegheny-Ludlum Steel Co.	S, P, T												
	Allegheny-Ludlum Steel Co.	B, F, C, S, P												
Austenitic	Allegheny-Ludlum Steel Co.	S, P, B, F	0.08 Max	13.5-16	24-27		0.35 Max	1.9-2.3	1.0-1.75			0.4-1.0	1-2	V, 0.1-0.5 B, 0.003-0.01 P, 0.25
	Crucible Steel Corp.	P, B, billets	0.30	18.5	9.5							0.50	3.5	

(a) Forms: B - Bar

F - Forging

C - Casting

S - Sheet

P - Plate

W - Wire

T - Tubing

E - Extrusion

(b) Composition of castings may be altered slightly from nominal

These steels also have been treated in detail in Defense Metals Information Center reports by D. C. Ludwigson and A. M. Hall [5] and by A. F. Hoenie and D. B. Roach [6].

In the vast majority of applications for which the precipitation-hardenable stainless steels are selected, the combinations of properties inherent in these materials fit them to serve successfully. Accordingly, they are usually placed in service without any special surface preparation. Depending on the particular application, machined, cold-rolled, pickled, ground, polished, or buffed finishes generally are adequate. In fact, the intent of such surface preparation as may be used is to insure that the condition of the material's surface does not detract from the performance of the steel, but instead, permits the material's inherent characteristics to be effective. As a general rule, then, surface treatments that can be described as coatings, or those that are mechanical in nature, are not applied to the precipitation-hardenable stainless steels.

On the other hand, there are certain instances in which the precipitation-hardenable stainless steels are given special surface treatments of the coating, as well as of the mechanical, type. On occasion, these steels are hard surfaced, electroplated, carburized, and nitrided. Likewise, they may be given such surface mechanical treatments as burnishing, planishing, and peening. However, because these steels are not used at high temperatures, they are not known to be given aluminum-containing, ceramic, or other heat-resistant diffusion coatings. The semiaustenitic types are seldom used above 700° F (638° K), while the martensitic varieties may see service temperatures up to perhaps 900° F (748° K) and the austenitic steels up to 1300° F (968° K).

It is the purpose of this report to discuss illustrative cases where the precipitation-hardenable stainless steels are, or may be, given a surface treatment, as well as instances of surface treatments or conditions to be avoided.

COATING TREATMENTS

Hard Surfacing

During the past few years a limited amount of hard-facing experience has been gained with some of the precipitation-hardenable stainless steels. For example, in a brief program conducted for the Columbus Division of North

American Aviation, Inc., by Battelle Memorial Institute it was found that AM-355 could be hard faced successfully with Colmonoy No. 6* [7] hard-facing material if the operation were carried out in a dry hydrogen atmosphere [8]. When an endothermic furnace atmosphere was used, the Colmonoy material would not fuse to the base metal, presumably because of the development of an oxide film that interfered with the operation. The hard-facing alloy was in powder form and was applied to the AM-355 base metal by spraying with a metal spray gun, after which the work was brought to a temperature of 1900° F (1298° K) to fuse the coating to the base metal.

Arresting-gear hook points for the A3J and T2J aircraft have been made of 17-4 PH forgings hard surface with Colomonoy No. 6 [9]. The 17-4 PH steel was chosen for its strength, toughness, and corrosion resistance; the hard-facing material provided improved wear resistance on selected critical surfaces. Originally, the coating was fused at 1900° F (1298° K) in a vertical retort furnace supplied with a pure, dry hydrogen atmosphere. The procedure was to apply the coating with a metal spray gun, load the coated work into the retort, purge the retort, raise the temperature to 1900° F (1298° K), hold for 10 min, remove the retort from the furnace, and allow it to cool in still air. The cooling time to 300° F (418° K) was a minimum of 90 mins. The hook points were then aged 4 hrs at 1150° F (886° K). However, on cooling to room temperature after the fusion step the coatings were found to be cracked, many of the cracks being readily visible to the unaided eye.

Investigation of the cracking phenomenon led to the conclusion that the cracking was due to the expansion (about 0.5 percent) that occurs in 17-4 PH when this alloy transforms from austenite to martensite [9]. This transformation begins at about 275° F (404° K). During the expansion of the base metal on transformation, the brittle hard-facing alloy would crack and the cracks would propagate through the coating and into the underlying diffusion zone. However, they would not continue into the unaffected base metal.

Because the cracking was brought about by factors inherent in the materials and was not attributable to procedural errors, it could not be eliminated without changing materials. However, it could be minimized considerably by reducing the time the hard-facing alloy was molten [9]. This could be done in a hydrogen muffle furnace so set up that the middle section was at fusion temperature while the front was somewhat cooler. The work could be preheated

* The nominal composition of Colmonoy No. 6 is
0.75C, 16.0Cr, 3.5B, 4.5Fe, 4.5Si, Bal. Ni [7].

in the front, then moved to the middle, and held there only for the minimum time required to cause fusion. This procedure would result in a very shallow diffusion zone beneath the hard coating, and the amount and severity of cracking would be greatly reduced.

Another method of reducing the time the hard-facing alloy was molten was to fuse the material with an oxyacetylene torch [9,10]. When this method was used, the hard-facing material was changed from Colmonoy No. 6 to Metco 16C* [11], the latter being less fluid at its fusion temperature than the former. Because of its fluidity, the Colmonoy No. 6 was difficult to torch fuse on large curved parts such as hook points.

In torch fusing, the sprayed parts were uniformly preheated to about 1400° F (1023° K) either in a furnace or by means of an oxyacetylene torch [12]. Fusion was then accomplished with as little further heat input from the torch as possible. On completion of the operation the part was allowed to cool to room temperature in still air.

Torch-fused parts were found to respond nonuniformly to the subsequent aging treatment. This was not surprising as the metal just beneath the coating would have reached the melting point of the hard-surfacing alloy, about 1900° F (1298° K), during the fusing treatment, while the rest of the part would have experienced successively lower temperatures down to some 1400° F (1023° K). Resolution annealing before aging was clearly indicated. The recommended solution annealing temperature for 17-4 PH is 1900° F (1298° K). However, to use this temperature would defeat the purpose of torch fusing. Holding 30 min at 1800° F (1243° K) and air cooling, followed by aging 4 hr at 1150° F (886° K), was found to be a satisfactory heat treatment.

Recent communications with Wall Colmonoy Corporation confirm the inevitability that cracking will occur in hard surfacing coatings fused to 17-4 PH on cooling to room temperature after the fusing operation [13,14]. Of course, such coatings will crack when fused to any alloy that undergoes an austenite-to-martensite transformation on cooling from the fusing temperature to room temperature. However, when service conditions involve essentially pure wear, the presence of small cracks in the coating is tolerable.

* The nominal composition of Metco 16C is
0.25C, 16.0Cr, 4.0B, 2.5Fe, 4.0Si, 3.0Cu, 3.0Mo, Bal. Ni [11].

Another precipitation-hardenable stainless steel that has been used for aircraft arresting-gear hook points, after hard facing the wearing surfaces, is A-286 [15]. This steel has been hard surface with Colmonoy alloys as well as with materials prepared by the Metallizing Engineering Company. Fusion has been accomplished both by heating in a controlled atmosphere furnace and by means of an oxyacetylene torch.

Electroplating

General Discussion. A great many aircraft and spacecraft components are electroplated with a variety of metals and for a number of reasons. The metals most frequently used as coatings for these parts are gold, copper, nickel, chromium, silver, cadmium, and zinc. Some of the reasons for using electroplated coatings in aerospace applications are to prevent tarnish and corrosion, increase wear and abrasion resistance, prevent seizing and galling, and control the temperature of the component.

Gold plate is used principally because of its favorable energy absorptance and emittance characteristics; in addition, gold is highly corrosion resistant [16]. Nickel plate is adherent, corrosion resistant, and can be quite hard as deposited. Hardness can be varied from about 150 to some 800 Vickers [17]. Black nickel, which usually is an alloy containing up to 48 percent zinc along with sulfur and organic inclusions, is often applied to interior surfaces to increase heat absorption, reduce heat reflection, or promote uniformity of temperature in a component or assembly [16,18]. Zinc, copper, and silver are often employed as substrate barrier coatings [16]. Cadmium has good corrosion resistance and nongalling properties [19]. Industrial chromium plates are hard (up to 1100 Vickers), are corrosion resistant, have a low coefficient of friction, and possess excellent nongalling and nonwetting properties [17]. A summary of the characteristics of these and other electrodeposited metallic coatings is given in Table II [19].

Electroplates can be deposited on a host of metals and alloys. For aerospace applications requiring electroplating, the most common basis metals are aluminum and its alloys, magnesium and magnesium alloys, low-alloy steels, and (less frequently) stainless steels and nickel-base alloys [16,20]. Generally, however, nickel alloys and stainless steels, especially the precipitation-hardenable stainless steels, either are not used in applications where plating is suitable or required, or they do not need to be plated because they inherently possess the corrosion resistance or other attribute that plating would be designed to supply.

TABLE II. (Cont'd)

Physical and Mechanical Properties												
Plate (4)	Usual Basis Metals	Thermal			Electrical Resistivity microhm, cm percent at 5000 A	Reflectance (polished), percent at 5000 A	Hardness	Abrasion Resistance	Adhesion	Appearance	Cost	Thickness, mil
		Melting Point, °F (°K)	Conductivity Btu hr sq ft °F ft (joule m sec K)	Resistivity microhm, cm percent at 5000 A								
Lead	Ferrous metals, copper	621 (395)	20.1 (34.5)	22.6	Low	5 Bhn	Poor (but alloy coatings have good bearing properties)	Good	Good	Gray	Low	0.5-8 (wear) to 50 (corrosion) (15 x 10 ⁻⁶ to 15 x 10 ⁻⁴)
Nickel	Most ferrous, non-ferrous metals	2651 (1711)	34.4 (58.2)	7.4-10.8	61	140-500 DPH	Good-very good	Very good	Very good	White, either dull or bright	Moderate	0.1-1.5 (decorative) (3 x 10 ⁻⁷ - 45 x 10 ⁻⁶) 5-20 (industrial) (15 x 10 ⁻⁶ - 6 x 10 ⁻⁴) up to 0.25 in. (0.635 cm) (electroforming)
Palladium	Copper and its alloys plus underplate of silver, gold or platinum	2850 (1804)	40.6 (69)	11	72 ^(b)	255-265 Knoop	--	Careful processing needed to prevent peeling	Careful processing needed to prevent peeling	White, tends to tarnish	High	0.02-0.2 (6 x 10 ⁻⁷ - 6 x 10 ⁻⁶)
Platinum	Gold, Copper alloys	3223 (2026)	40.2 (68.5)	10	58	280-290 Knoop	Poor	--	--	Bright gray, darker than rhodium or silver	High	Flash up to 2 (6 x 10 ⁻⁵)
Rhenium		5732 (3406)	--	21	--	250 Bhn	--	--	--	Bright gray	High	--
Rhodium	Most ferrous, non-ferrous metals	3553 (2207)	50.9 (85)	4.7	76	400-800 Bhn	High	Good	Good	Mirror-bright white	Moderate	0.001-1 (3 x 10 ⁻⁷ - 3 x 10 ⁻⁶)
Silver	Most ferrous, non-ferrous metals	1760 (1221)	244 (422)	1.6	91	50-150	Good	Good	Good	Bright white	High	0.1 (with undercoat) to 1 (3 x 10 ⁻⁷ to 3 x 10 ⁻⁶)
Tin	Usually ferrous metals	448 (499)	36.3 (62.8)	11.5	54 ^(b)	5	Poor unalloyed	Good	Good	Bright white	Moderate	0.015-0.5 (45 x 10 ⁻⁸ - 15 x 10 ⁻⁶)
Zinc	Usually ferrous metals	786 (685)	64.2 (111)	5.8	55	40-50	Poor	Excellent	Excellent	Matte gray to bright	Low	0.1-0.5 (light duty) (3 x 10 ⁻⁷ - 15 x 10 ⁻⁶) 0.3-2 (outdoors) (15 x 10 ⁻⁶ - 6 x 10 ⁻⁵)
Cobalt-Nickel		--	--	--	--	350-450 DPH	Very good	Good	Good	Gray	Moderate	0.1 (3 x 10 ⁻⁷)
Copper-Tin (Bronze)	Steel, copper, brass, zinc	--	--	--	High	150-250 DPH	Good	Excellent	Excellent	Bright pink	Low	0.5 (15 x 10 ⁻⁶)

TABLE II. (Cont'd)

Plate ^(a)	Usual Basis Metals	Physical and Mechanical Properties									
		Melting Point, °F (°K)	Thermal Conductivity Btu hr sq ft F ft (joule m sec ⁻¹ K)	Electrical Resistivity microhm cm (percent at 5000 A)	Reflectance (polished)	Hardness	Abrasion Resistance	Adhesion	Appearance	Cost	Thickness, mil ($\times 10^{-3}$)
Copper-Zinc (Brass)	Iron, steel, aluminum, zinc	--	--	--	High	Soft	Poor	Excellent	Bright yellow at 10 ⁻⁵ in. Yellow at 20 ⁻⁵ in.	Low	0.1 (3×10^{-2})
Lead-Tin	Steel, copper, brass	--	--	--	--	Soft	Poor	Good	White	Low	0.2 (6×10^{-2})
Tin-Nickel	Most ferrous, non-ferrous metals	--	--	--	15-118	62.5 Vickers	Good	Good over copper or bronze undercoat	Bright white	Moderate	0.5 (15×10^{-2})
Tin-Zinc	Most ferrous, non-ferrous metals	--	--	--	--	Similar to tin	Good	Good	White	Moderate	0.15 (4.5×10^{-2})

(a) At 10 000 A.

TABLE II. (Cont'd)

Plate	Important Characteristics
Aluminum	Corrosion resistant; good thermal - and heat-resistance properties when diffused into base metal. Infrequently used; can substitute for hot-dipped aluminum.
Antimony	Tarnish resistance, pleasing appearance when polished. However, coatings too brittle for practical application.
Arsenic	Infrequently used to provide decorative antique effect.
Bismuth	Somewhat expensive. Infrequently used for corrosion protection.
Cadmium	Pleasing appearance, provides good corrosion protection indoors on iron and steel. Less apt to darken and form corrosion products than zinc; nevertheless, zinc is more widely used because of cost. Outdoor corrosion resistance varies and should be checked by testing. Radio, television, and electronic chassis; aircraft, marine, and military outdoor use; washing equipment, steel embedded in concrete, and similar parts.
Chromium	Excellent resistance to wear, abrasion, and corrosion. Low coefficient of friction and high reflectivity. Popular decorative corrosion-resistant coating on automobile exterior and interior trim, appliances, and business machines. Widely used in bearing applications and to build up worn surfaces.
Cobalt	Similar to nickel, but more expensive. Infrequently used alone except for applications where high hardness is needed and on mirrors and reflectors. Frequently used in alloy electroplates to upgrade properties.
Copper	Good appearance (when polished and/or lacquered) and corrosion resistance; high electrical and thermal conductivity. Undercoat to improve adhesion and protective ability of subsequent electroplates (e. g., nickel and chromium) or to prevent hydrogen embrittlement. Also used as wire coatings, stop-off coatings during heat treatment and chemical milling, lubricant during drawing, thermally conductive coatings on cooking utensils, and for electroforming.

TABLE II. (Cont'd)

Plate	Important Characteristics and Uses
Gold	Resistant to tarnishing, chemical attack, and high-temperature oxidation. Good ductility, thermal reflectivity and electrical conductivity. Pen points, jewelry, watch and vanity cases, musical instruments, reflectors, nameplates, eyeglass frames, bracelets, trophies, novelties, electrical contacts, springs, waveguides, various electronic parts, laboratory apparatus.
Indium	Tarnish resistant, malleable, and ductile. Principally used as an overlay diffusion coating on silver-plated steel bearings for high-speed aircraft engines. Also used as an alloying element to upgrade mechanical properties of alloy coatings.
Iron	Can be deposited with selected properties; easily fabricated and plated over; high purity. Build-up of undersized parts, electrotypes, electroforming of molds.
Lead	Resistant to many acids, hot corrosive gases, and corrosive atmospheres. Lead normally deposited by hot dipping; however, lead electroplates are used to protect chemical equipment, brine refrigerating tanks, metal gas shells, nuts and bolts, and storage battery parts.
Nickel	Excellent appearance, and resistance to a wide variety of chemicals and corrosive atmospheres; can be electroplated in range of hardness (soft to hard). Decorative applications either alone or as a heavy base for thin chromium electroplates to improve corrosion resistance and mechanical properties, as in trim for automobiles, appliances, business machines, and consumer goods. Also used for electroforming, and to build up worn and mismachined parts.
Palladium	Good appearance, tarnish and corrosion resistance. Ornamental and decorative applications. Can be used alone or under rhodium for radar and electronic equipment.

TABLE II. (Cont'd)

Plate	Important Characteristics and Uses
Platinum	Good appearance, tarnish and corrosion resistance. Ornamental ("white gold") applications and as a flash decorative coating. Also to protect surfaces that must withstand unusual corrosive environments.
Rhenium	Although melting point is high, begins to oxidize as low as 752 F. Poor resistance to moisture. Infrequently used but has been proposed for electronic applications such as cathode and filament emitters and heater wires.
Rhodium	Brilliant white color, tarnish and corrosion resistant, good electrical conductivity. Decorative and tarnish-resistant finish for costume jewelry, insignia, emblems, musical instruments, medical and surgical parts, laboratory equipment, and optical goods. Also electrical contacts, reflectors and mirrors.
Silver	Excellent appearance when suitably prepared and protected, high load-carrying capacity and electrical conductivity, good resistance to many chemicals. Decorative applications such as tableware, hollow-ware, cigarette lighters, and musical instruments. Also industrial applications, such as bearings, surgical instruments, chemical equipment, electrical contacts, etc., where conductivity is needed.
Tin	Corrosion resistant, attractive appearance, hygienic, easily soldered, soft and ductile, good bearing properties. Food and beverage containers, refrigerator evaporators, food and dairy equipment, hardware, appliance and electronic parts, copper wire, and bearings.
Zinc	Easily and rapidly applied, high corrosion resistance. Electrogalvanized sheet is widely used in fabricating appliance and automotive parts. Also, for finishing small parts such as pipe couplings, bolts, nuts, rivets, washers, nails, hinges, hangers, hooks and buckles. Larger parts include electrical conduit pipe, silo and tie rods, screening, telephone exchange equipment, and iron and steel castings.

TABLE II. (Concluded)

Plate	Important Characteristics and Uses
Cobalt-Nickel	Wide range of magnetic properties. Magnetic recording, permanent magnet coating on memory drums in digital computers. Electroforming.
Copper-Tin (Bronze)	Red-bronze coatings (lacquered to prevent tarnishing) used on inexpensive jewelry, door plates, hardware, trophies, handbag frames; as undercoat for nickel and chromium; as stop-off coating in selective nitriding of steel; also used on bearing surface. Speculum coatings (40-50% tin) used for tableware and household fixtures; not recommended for outdoor use.
Copper-Zinc (Brass)	Rich appearance much like solid brass. Little resistance to outdoor atmospheres; may require lacquer coating to resist indoor tarnishing. Decorative applications such as lamps and trays; low-cost trim, interior automotive hardware, tubular furniture, household goods, toys casket hardware, novelties. Also used to promote adhesion of rubber to steel.
Lead-Tin	Harder and more protective than lead; good friction and bearing properties. Heavy duty bearing where corrosion protection is needed, and as an aid in soldering.
Tin-Nickel	Good decorative properties (resembles chromium); high resistance to tarnishing, common reagents, and marine corrosion; good bearing and oil retention properties; solderable. Plating baths have outstanding throwing properties. Cooking utensils, analytical weights and surgical instruments, numerous watch parts, chemical pumps, valves and flow control devices.
Tin-Zinc	Good corrosion resistance, excellent solderability, tendency to fingermark (can be prevented by lacquering). Radio and television parts, cable connectors, relay assemblies, galvanic protection of steel parts contacting aluminum.

A few specific instances of the electroplating of precipitation-hardenable stainless steels have been identified and deserve mention here. For example, billets of A-286 austenitic precipitation-hardenable stainless steel and PH 15-7Mo semiaustenitic precipitation-hardenable stainless steel have been electroplated with a 0.04-in. (0.1-cm) thick layer of nickel prior to hot extrusion with standard glass lubricants [21]. The objective was to prevent tearing and scoring of the surface of the extruded shapes. It was found, however, that by using proper die design and a preheated container the nickel plate was unnecessary. In fact, in the case of the PH 15-7Mo material, the nickel plate detracted from the strength obtainable on subsequent heat treatment. During extrusion, the nickel plate diffused into the surface layers of the stainless steel, increasing the stability of these layers to the point that they would not transform to martensite and harden during subsequent hardening and aging heat treatments.

Again, A-286, which is difficult to braze, can be brazed readily when plated with nickel or iron. Such titanium- or aluminum-containing alloys form an adherent oxide film on the surface, which cannot be reduced even by an extremely pure, dry-hydrogen, brazing atmosphere. This film is a great impediment to brazing. However, plating with nickel or iron, whose oxides are easily reduced, overcomes the problem [22]. Also, it has been found that high-strength precipitation-hardenable stainless steel parts of missiles housed in underground silos can be protected from stress-corrosion cracking by nickel-cadmium electroplating [23]. This treatment has been given to parts that could not be adequately stress relieved.

Most of the plates discussed above and listed in Table II probably can be electrodeposited on the precipitation-hardenable stainless steels, although information on the subject is extremely meager. In general, each metal can be plated from several baths of different types and compositions, each bath having its own range of applicability and its own set of operating conditions. Thus, electroplating is a broad and complex technology, and a detailed treatment of the subject is beyond the scope of this report [24,25,26].

In the absence of information bearing directly on procedures for plating the precipitation-hardenable stainless steels it can be assumed, as a point of departure, that they behave much like their nonage-hardenable counterparts. Thus, such martensitic precipitation-hardenable stainless steels as 17-4 PH and 15-5 PH would be expected to perform in a manner similar to that of

AISI 410, 414, 416, or 420. Likewise, austenitic precipitation-hardenable stainless steels such as A-286 and HNM would be expected to behave about like other highly alloyed austenitic stainless steels. With the semiaustenitic types, such as 17-7 PH, PH 15-7Mo, PH 14-8Mo, AM350, and AM355, the situation would appear to be more complicated. As solution annealed, these steels are austenitic and therefore should resemble the AISI 300 series of austenitic stainless steels. As hardened, on the other hand, they possess a martensitic matrix which would tend to make them take on some of the attributes of the martensitic stainless steels. However, they are more highly alloyed and enjoy corrosion and passivity characteristics approaching those of the AISI 300 series of austenitic stainless steels.

Activation. Thus, in common with other stainless steels, the precipitation-hardening types tend to be passive, that is, they tend to possess oxygen-containing films on their surfaces. These films interfere with the adherence of electroplates and must be removed before electroplating. This film-removal step, which is called activation, distinguishes the stainless steels from most other metals and alloys in the technology of electroplating. Activation is carried out after descaling or other surface preparation as well as after such steps as wiring, jigging, masking, and final cleaning, and is the step immediately preceding plating. Activation treatments for stainless steels are as follows [26]:

a. Immersion treatments

1. Immerse in 20 to 50 percent sulfuric acid at 130° to 150° F (325° to 336° K) for at least 1 min after gassing commences. It may be necessary to start the gassing by touching the stainless steel with a piece of carbon steel.
2. Immerse for 26 sec at room temperature in:

Hydrochloric acid	0.1 percent
Sulfuric acid	1.0 percent

b. Cathodic treatments

1.

Sulfuric acid	5-50 percent
Temperature	Room
Current density	5 amps/ft ² (53.5 amps/m ²)
Time	1-5 min

- | | |
|----------------------|--|
| 2. Hydrochloric acid | 5-50 percent |
| Temperature | Room |
| Current density | 20 amps/ft ² (214 amps/m ²) |
| Time | 1-5 min |
3. Immerse in 10 to 30 percent hydrochloric acid at room temperature followed by cathodic treatment in:
- | | |
|-----------------|---|
| Sulfuric acid | 5-50 percent |
| Temperature | Room |
| Current density | 5-25 amps/ft ² (53.5-267.5 amps/m ²) |

c. Simultaneous Activation - Plating Treatments

- | | |
|--------------------|--|
| 1. Nickel chloride | 32 oz/gal (240 kg/m ³) |
| Hydrochloric acid | 11 fl oz/gal (8.58 x 10 ⁴ cm ³ /m ³) |
| Temperature | Room |
| Electrodes | Nickel |

First, treat anodically at 20 amps/ft² (214 amps/m²) for 2 min, followed by cathodic treatment at 20 amps/ft² (214 amps/m²) for 6 min.

- | | |
|--------------------|--|
| 2. Nickel chloride | 32 oz/gal (240 kg/m ³) |
| Hydrochloric acid | 16 fl oz/gal (1.25 x 10 ⁵ cm ³ /m ³) |
| Temperature | Room |
| Anodes | Nickel |

First, treat cathodically at 50 to 200 amps/ft² (535 to 2140 amps/m²) for 2 to 4 min, then reduce to 15 to 50 amps/ft² (160.5 to 535 amps/m²) for 15 to 30 min.

- | | |
|--------------------------|--|
| 3. Nickel chloride | 4-40 oz/gal (30-300 kg/m ³) |
| Hydrochloric acid | 2-20 fl oz/gal (15610-156100 cm ³ /m ³) |
| Temperature | Room |
| Anodes | Nickel |
| Current density-cathodic | 5-100 amps/ft ² (53.5-1070 amps/m ²) |

4. Hydrochloric acid	Concentrated
Copper sulfate	0.05 oz/gal (0.376 kg/m ³)
Temperature	Room
Anodes	Nickel
Current density-cathodic	40-60 amps/ft ² (428-624 amps/m ²)
Time	1-5 amps/ft ² (10.7-53.5 amps/m ²)
5. Nickel sulfate	32 oz/gal (240 kg/m ³)
Sulfuric acid	6.7 oz/gal (50.4 kg/m ³)
Temperature	86-104° F (300-310° K)
Anodes	Lead
Current density-cathodic	150 amps/ft ² (1605 amps/m ²)
Time	5-10 min

After activation, the work is rinsed and transferred to the plating bath as quickly as possible. The rinse water should be acid (pH 2.5-3.5). The drag-over of acid from the activation treatments will frequently make the rinse water sufficiently acid. If possible, the current should be on as the parts are immersed in the plating solution.

Depending on the type of stainless steel and activating treatment, adherent deposits of most metals can usually be deposited directed on the activated surface. In particular, Treatment c-2 is recommended for the activation of stainless steels prior to plating with cadmium or nickel [25]. Except in the case of chromium plating, the use of a simultaneous activation-plating treatment usually gives more consistently good adhesion [26].

For chromium plating on stainless steel, the immersion treatment, a-2, has been used with success for activation of the basis metal [26]. However, it is common practice to eliminate activation as a separate step. Instead, the cleaned and rinsed work is placed directly in the chromium-plating solution where it is treated as an anode at 100 amps/ft² (1070 amps/m²) for a few minutes, after which the polarity is reversed and plating proceeds [26,27].

On the other hand, in Great Britain activation of stainless steels prior to chromium plating often is accomplished by using Treatment a-1 followed by a nickel strike, i. e., the deposition of a very thin layer of nickel in the order of 10×10^{-6} to 50×10^{-6} in. (25×10^{-6} to 127×10^{-6} cm) in thickness. The strike solution consists of 36 oz/gal (270 kg/m³) nickel sulfate and 4.3 oz/gal

(32.4 kg/m³) sulfuric acid. The current density is 150 to 200 amps/ft² (1605 to 2140 amps/m²), the plating time 5 to 10 min, the operating temperature 100° F (308° K), and either lead or nickel anodes may be used [20]. Alternatively, the parts may be given an anodic/cathodic treatment at room temperature in a solution of 38.5 oz/gal (290 kg/m³) nickel chloride and 13.6 oz/gal (102 kg/m³) hydrochloric acid using nickel electrodes. The anodic treatment is 2 min at 30 amps/ft² (321 amps/m²), then the current is reversed and the parts are plated 5 to 6 min at 30 to 100 amps/ft² (321 to 1070 amps/m²) [20].

Hydrogen Embrittlement. In such operations as pickling, cathodic cleaning, and electroplating, atomic hydrogen is produced on the surfaces of the work. The bulk of this atomic hydrogen combines to form molecules of hydrogen which go off as a gas. However, some atomic hydrogen is available to diffuse into the metal. Many metals and alloys, including the austenitic stainless steels, are not greatly affected when they absorb hydrogen. On the other hand, ferritic and martensitic steels tend to embrittle and often display the phenomenon of delayed, brittle failure on absorption of hydrogen. Included in this category are the martensitic precipitation-hardenable stainless steels as well as the semiaustenitic precipitation-hardenable stainless steels when in the hardened (martensitic) condition [28].

The presence of hydrogen in these alloys tends to lower tensile elongation and reduction of area. In steels of relatively low strength, the ultimate tensile strength is unaffected or sometimes slightly increased. In ultrahigh-strength steels, the ultimate tensile strength is reduced. In fact, under given conditions of hydrogen entry, the higher the original strength of the steel, the more drastic is the reduction in strength. The reason is that the ductility is decreased to such low values that the fracture strength of the steel is reached before the metal has the opportunity to strain harden itself to its original ultimate tensile strength [29].

Hydrogen embrittlement is most severe at intermediate temperatures, generally in the range of -150° to +210° F (171° to 389° K), and at low strain rates. Because of the latter factor, notch-bar impact tests do not reveal hydrogen embrittlement [29].

Hydrogen embrittlement often manifests itself in the form of delayed, brittle failure which occurs when the part is under a sustained tensile or bending load. This phenomenon is especially serious because, other things equal, the minimum stress for failure decreases as the strength level of the steel is

increased and because the failures occur with no appreciable ductility even though in a standard tensile test the hydrogen-bearing material may exhibit normal ductility [29].

These comments are made to caution the reader that the formation of hydrogen on the surface of precipitation-hardenable stainless steels in the martensitic condition, during electroplating and related operations, may lead to hydrogen-embrittlement problems. Detailed information on the complex subject of hydrogen in steel can be obtained from the literature [29, 30, 31, 32].

A common source of hydrogen embrittlement is the deposition of cadmium from a cyanide solution. Hydrogen embrittlement is even more likely to occur as a result of zinc plating from a cyanide solution. In fact, parts having very high strength may fail in the course of being zinc plated and it may be necessary to use some other plate or to avoid plating entirely. Other sources of hydrogen include highly acid pickling baths, cathodic cleaning operations, and nickel-strike baths [25].

By adhering to the following procedures, wherever possible, hydrogen embrittlement can be eliminated or considerably reduced in severity [25]:

1. Use mechanical descaling methods in preference to strong acid solutions.
2. If pickling is essential in preparing medium and high-strength parts, bake parts at about 375° F (459° K) for at least 3 hr after pickling and before plating.
3. In cadmium plating, use a porous deposit rather than a dense one, and bake parts at 375° F (459° K) for 3 to 24 hr as soon after plating as possible. The shorter baking periods are adequate for parts with tensile strength less than 220 000 lb/in² ($151\,668 \times 10^4$ N/m²); use the longer times for parts having tensile strength exceeding 220 000 lb/in² ($151\,668 \times 10^4$ N/m²).
4. In plating high-strength parts, avoid nickel-strike solutions and other solutions that are inefficient. A great deal of hydrogen is generated in these solutions which is available to embrittle the work.

In addition, ultrahigh-strength-steel parts should be free of surface stresses before electroplating operations, especially hard chromium plating. Thus, after grinding or other operations that cold work the surface, a low-

temperature stress relieving treatment may be advisable. When ultrahigh-strength parts are destined for service under dynamic loads, shot peening of the surfaces is recommended prior to chromium plating. Hard chromium plating tends to set up undesirable surface tensile stresses which are counteracted by the compressive stresses introduced by the shot peening operation. In some cases, it may be advisable to shot peen before chromium plating and bake afterwards [25].

Electroless Plating

Autocatalytic or electroless plating made its appearance in 1946. At that time, announcement was made of a process invented by Brenner and Riddell for plating nickel by making use of a spontaneous autocatalytic chemical reaction. Since then, the technology of this type of plating process has advanced, and it is now possible to deposit nine different metals singly or in combination. The metals that have been plated are: cobalt, chromium, copper, gold, iron, nickel, palladium, silver, and vanadium [33].

The term "electroless plating" was coined by the original inventors as a label for their process. However, it has since become more widely used and, in fact, is frequently used to designate other chemical plating processes in addition to the autocatalytic process. Thus, the term is sometimes applied to the salt-water gold process, contact plating processes, and immersion or replacement plating [34].

True electroless plating differs significantly from all other chemical plating processes. Not only does electroless plating require no electric current, it is the only chemical plating process that does not depend on the presence of a couple between galvanically dissimilar metals. Thus, no external connection is made to an active metal, as in the salt-water gold process; nor does the work contact any active metal in solution, as in contact plating; nor does the substrate dissolve, as in immersion plating [34].

In electroless plating, a catalytic substrate is immersed in an aqueous plating solution, whereupon the reaction begins spontaneously and metal is deposited only on the substrate surface. The deposited metal also catalyzes the reaction, causing it to continue autocatalytically. The essential ingredients of the plating solution are the metal ion and a reducing agent. Only certain metals have the required reduction potential and autocatalytic properties. In

addition to those listed earlier they are ruthenium, rhodium, osmium, iridium, and platinum [33]. In the plating reaction, the metal ion is reduced to the corresponding metal by receiving the required electrons, which become available upon the oxidation of the reducing agent. Such reductants as hypophosphite ion, borohydride ion, hydrazines, formaldehyde, and boranes have been employed [33].

Another important constituent of the plating solution is a compound, frequently the salt of an organic acid, which acts both as a buffer and as a complexing agent for the metallic ion. Buffering is important because the pH of the bath has a strong influence on its operation and the pH tends to change during bath operation. The function of complexing is to help control the availability of the metal ion to encourage plating only on the substrate, and discourage the formation of sludges and the spontaneous decomposition of the bath [34].

Electroless plating of nickel is now a thoroughly commercial process; the plating of other metals by this method is not so well advanced. Compositions of solutions for depositing electroless nickel are given in Table III [35]. The deposits are not pure nickel but are actually alloys that usually contain 4 to 8 percent phosphorus. The presence of the phosphorus makes the deposits harder, more corrosion resistant, and less magnetic than electrodeposited nickel. The hardness of electroless nickel as deposited is about 500 Vickers; when the plate is heated for an hour at 750° F (666° K) its hardness increases to some 700 Vickers. The deposits are reported to be brittle, but adherent and low in internal stress; they are smooth, semibright, and have a good appearance [35].

Other features of electroless plating, which apply particularly to electroless nickel plating, include the fact that the solutions have perfect throwing power and can deposit uniformly thick coatings on articles of complex shape. Also, the deposits are more pore-free than electroplates. Again, nonconductive surfaces can be easily sensitized to permit electroless plating [33].

Electroless nickel plate has been used on certain aircraft parts because of its hardness, wear resistance, and low level of internal stress. The heat-treated deposit has been preferred for its superiority in these respects to the as-deposited plate [36]. In addition, heat-treated electroless nickel deposits are often used as undercoatings beneath gold electroplates on satellite and other aerospace components formed from magnesium and aluminum [16].

No specific uses of electroless plates as coatings for precipitation-hardenable stainless steels have been identified. However, it has been reported that the deposition of a 1-mil (0.00002-m)-thick layer of electroless nickel,

TABLE III. TYPICAL COMPOSITIONS OF BATHS FOR DEPOSITING ELECTROLESS NICKEL

All baths are operated at 194° to 212° F (360° to 370° K), except Bath 8, 145° to 167° F (334° to 345° K) and Bath 6, 176° F (350° K).

Constituents of Baths, g/l	Acid Baths							Ammoniacal Baths	
	Hydroxy Acid Baths			Fluoride Baths				Citrate	Pyrophosphate
	1 (a)	2	3	4	5	6	7		
Nickel chloride, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	30	30	26	30 (c)	24	10 (d)	30	25 (c)	
Sodium hypophosphite, $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$	10	10	24	30	24	20	10	25	
Sodium citrate, $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 3-1/2\text{H}_2\text{O}$	--	15	--	--	--	10	100	--	
Sodium pyrophosphate, $\text{Na}_4\text{P}_2\text{O}_7$	--	--	--	--	--	--	--	50	
Hydroxyacetic acid	35	--	--	--	--	--	--	--	
Lactic acid	--	--	27	--	--	--	--	--	
Propionic acid	--	--	2.2	--	--	--	--	--	
Succinic acid	--	--	--	--	7	--	--	--	
Sodium acetate	--	5	--	--	--	--	--	--	
Ammonium chloride	--	--	--	--	--	--	50	--	
Ammonium fluoride	--	--	--	15	5 (e)	(f)	--	--	
Lead ion	--	--	0.002	--	--	--	--	--	
Alkali for neutralizing pH	NaOH 4-6	NaOH 4-6	NaOH 4.6	?	--	--	NH ₄ OH 8-10	NH ₄ OH 10-11	
Rate of deposition, μ hr	15	7	20	30	15	30	5	15	

(a) This bath is referred to as "Hydrac," which is a contraction of "hydroxyacetic."

(b) Bath patented by General American Transportation Co.

(c) $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$

(d) Basic nickel carbonate, $2\text{NiCO}_3\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$.

(e) Sodium fluoride.

(f) 70% HF solution, 5 ml 1: KF, 10 g 1: NH_4HF_2 , 25 g 1.

followed by baking to remove any absorbed hydrogen, offers almost complete protection to these steels against stress-corrosion cracking [37].

Carburizing and Decarburizing

All stainless steels, including the precipitation-hardenable types, can be carburized; that is, they are capable of absorbing carbon when conditions are reducing, carbon is chemically available, and the temperature is high enough. However, very rarely are such steels carburized intentionally because the process usually is extremely detrimental to corrosion resistance and other properties.

During carburizing or during cooling from the temperatures at which carburizing occurs, the carbon that has diffused into the surface layers of the metal combines with chromium in the steel to form a precipitate of chromium carbide particles. Chromium thus combined and precipitated is unavailable to protect the steel from corrosion. Moreover, when the chromium carbide particles are dispersed as continuous networks along grain boundaries, they form myriad galvanic cells with the adjacent chromium-depleted matrix, further reducing the corrosion resistance of the steel and, in particular, rendering the material susceptible to intergranular corrosion. In addition, the very presence of the intergranular carbide networks reduces the ductility and toughness of the steel.

The austenitic and semiaustenitic stainless steels are especially prone to develop such intergranular chromium carbide networks. With the martensitic types, there is a greater tendency toward the formation of random dispersions of chromium carbide particles. Consequently, they often are not so susceptible to intergranular attack, but may become quite prone to stress-corrosion cracking as well as to general corrosive attack in relatively mild environments.

Sources capable of supplying carbon to carburize the precipitation-hardenable and other stainless steels include grease, oil, coal, coke and coal dust, bone black, cast iron turnings, asphalt, tar, methane and other hydrocarbons, molten salts containing additions of carboniferous rectifiers such as cyanide compounds to make them neutral toward medium carbon and tool steels, and many of the gaseous atmospheres used to case harden standard carburizing steels [38]. Temperatures in the range of 1400° F (1013° K) and upwards are conducive to the carburization of these steels.

Occasionally, such martensitic precipitation-hardenable stainless steels as 17-4 PH and 15-5 PH are gas carburized to improve resistance to wear and galling [39]. The treatment temperature often is quite high, ranging up to 1850° F (1271° K). The resulting microstructure is rather unique. The surface layer is composed of hard carbides in an austenitic matrix beneath which is a layer of soft, ductile, carbide-free austenite, while below that is the normal martensitic structure of the uncarburized core. The key factor in the development of this structure is the fact that, during carburizing, sufficient carbon diffuses fairly deeply into the metal to form a stably austenitic sublayer which does not transform to martensite on cooling to room temperature.

In fact, the potency of carbon as an austenite stabilizer is another reason to avoid carburizing the semiaustenitic type of precipitation-hardenable stainless steel. The high-carbon surface layers produced by the carburizing treatment cannot be transformed subsequently to martensite and, therefore, will not develop the high strength that characterizes this type of steel when fully heat treated. The carburizing treatment, in effect, tends to convert the surface layers from being a semiaustenitic stainless steel to being a completely austenitic but nonstainless material.

To avoid the harmful effects of carburizing, the precipitation-hardenable stainless steels are usually heat treated in air. Electric or radiant tube, gas, and oil furnaces are especially satisfactory for this purpose [38,40]. The degree of oxidation produced in an air atmosphere normally is not detrimental, even when the heat treating temperature is as high as 1950° to 2000° F (1326° to 1353° K). Salt-bath equipment has been found to do an acceptable job, but the neutrality of the bath is sometimes difficult to control [40]. Heat treating in so-called neutral atmospheres, such as those composed of the products of combustion of fuels, is to be avoided [40]. These atmospheres are not neutral toward the precipitation-hardenable stainless steels. And the result of using them is the formation of very thin oxide films on the steel which are extremely difficult to remove. Likewise, the use of open fired gas or oil furnaces is not recommended unless the work is placed in a sealed retort. The products of combustion may contaminate the metals, unless their composition is carefully controlled [40].

When bright scale-free surfaces are required on the work, it is necessary to resort to special atmospheres. Bright annealing can be accomplished successfully in high purity hydrogen or argon with a dew point of -60° F (220° K) or lower [40]. Heat treatment in a vacuum also can yield an excellent surface condition provided the vacuum is in the order of 10 microns (0.00001 m) [40].

In cases where a thin scale can be tolerated but the amount of scaling that occurs when the metal is heat treated in air is unacceptable, a special protective coating may be applied to the part prior to heat treating. The majority of such coatings are proprietary; a listing of representative proprietary coatings appears in Table IV [41]. The primary purpose of these coatings is to minimize scaling during heat treating and to make subsequent scale removal by chemical means easier. Such coatings perform best when the coated part is heat treated in air, which allows the coating to oxidize and become an effective barrier between the atmosphere and the work. Because these coatings generally have organic binders, they tend to carburize the work if heated in a neutral or reducing atmosphere.

A case in point is the heat treatment of components made from 17-7 PH or PH 15-7Mo in thin gages [42]. The loss in the thickness of the part due to the scaling that occurs on heat treating in air is too great to be acceptable. On the other hand, to remove a thin oxide film by pickling invites preferential intergranular attack, sand blasting causes distortion of the component and work hardening of its surfaces, and vapor blasting is prohibitively expensive. Recourse is to have a protective coating. In the example cited, Turco 4367 was used. After heat treating, the component was immersed in an alkaline salt bath at 900° F (748° K) which conditioned the coating so that it could be removed readily by a subsequent flash pickle in a nitric-hydrofluoric acid solution.

On rare occasions, decarburization can present a problem. For example, in the course of manufacture, hemispheres spun from PH 15-7Mo sheet became sufficiently decarburized in repeated interstage anneals that they would no longer retain their soft, workable austenitic structure on cooling to room temperature [43]. The composition of the steel had become so unbalanced from loss of carbon that the material transformed to hard, unworkable martensite on cooling from the annealing temperature. In this case, decarburization had transformed the steel from a semiaustenitic to a martensitic precipitation-hardenable stainless steel. The material had been coated before each anneal. However, the atmosphere was composed of the products of combustion of fuel gas rather than air. Had it been air, the coating would have oxidized to a greater extent, becoming more impervious in the process, and thus more effective in preventing decarburization. In fact, in all probability, no coating whatever would have been required had the steel been annealed in air.

TABLE IV. PROPRIETARY COATINGS TO PROTECT STAINLESS STEELS DURING HEAT TREATMENT

Coating	Purpose	Supplier
Turco 4367	Minimize scaling. Facilitate scale removal. Prevent decarburization and carburization	Turco Products, Inc. P.O. Box 1055 Wilmington, California
Turco Pretreat	Inhibit formation of tenacious scales and intergranular oxidation	Turco Products, Inc. P.O. Box 1055 Wilmington, California
No-Carb	Prevent decarburization	Park Chemical Company 8074 Military Avenue Detroit, Michigan
Skalix	Oxidation inhibitor	Rinshed-Mason Company 1244 North Lemon Street Anaheim, California
Markal C-R	Prevent carburization, decarburization, oxidation, gas absorption	Markal Company 3052 West Carroll Avenue Chicago, Illinois
Chicago Vitreous Corporation Coatings (a)	Prevent carburization, scaling, decarburization, oxidation	Chicago Vitreous Corp. Div. of Eagle Picher Co. 1425 South 55th Street Cicero, Illinois
L. H. Butcher Coatings	Minimize scaling and decarburization	L. H. Butcher Company 15th and Vermont Street San Francisco, California

(a) This company does not merchandize coatings, but has developed ceramic coatings for its customers.

Nitriding

Because of their chromium content, all stainless steels can be case hardened to a greater or lesser degree by the process of nitriding. The chromium in the steel aids the diffusion of nitrogen into the material and facilitates the formation of a stable case possessing high hardness. Stainless steels are nitrided to obtain high surface hardness, to increase wear resistance, to develop antigalling properties, and to improve fatigue resistance [44].

On the other hand, nitriding tends to detract from the corrosion resistance of these steels in that the case usually has lower corrosion resistance than the basis material. The reason is that the nitrogen which is introduced by nitriding combines with the chromium in the surface layers to form chromium nitride, thus reducing the availability of this element to protect the steel from corrosion [39,44,45].

All three types of precipitation-hardenable stainless steel have been nitrided: the martensitic type represented by 17-4 PH and 15-5 PH; the semi-austenitic alloys, AM-350, AM-355, 17-7 PH and PH 15-7Mo; and the austenitic steel, A-286 [39,44,45,46]. The principal forms are finished parts produced from bar stock. Shafts for jet engine fuel pumps are examples of parts made of a precipitation-hardenable stainless steel and then nitrided; the steel used was 17-4 PH [47]. Case depths are generally in the order of 0.004 to 0.006 in. (0.01016 to 0.01524 cm) and surface hardness values of 67 Rockwell C or 900 DPH* are obtainable [39].

Nitriding of the precipitation-hardenable stainless steels is carried out by the gas nitriding method, the nitriding temperature being in the range of 925° to 1050° F (762° to 851° K). At such temperatures, these steels can be age hardened. Therefore, it is not uncommon to combine nitriding with the final aging treatment [39,45].

Before nitriding, the oxide film that protects the steel from corrosion must be removed. This may be done by such methods as wet blasting, pickling, or reduction in a suitable reducing atmosphere. Of course, the parts must be free of foreign particles, grease, oil, finger marks, and other contaminants [44].

* Diamond Pyramid Hardness

In general, single-stage nitriding cycles are used, the temperature being 975° to 1025° F (784° to 817° K), and the time ranging from 20 to 48 hr depending on the case depth required. The atmosphere is anhydrous ammonia [44].

In addition, a proprietary nitriding process known as Malcomizing* has been used to case harden precipitation-hardenable stainless steels [46,48]. This process is carried out on parts the surfaces of which have been carefully depassivated and cleaned after finish machining and heat treating. The process requires temperatures of 920° to 1050° F (759° to 831° K) and times of 6 to 8 hr. The recommended heat treatment to be used before Malcomizing and the case depths and hardnesses obtained for a number of precipitation-hardenable stainless steels are listed in Table V [46].

TABLE V. CASE HARDENING PH STAINLESS STEELS BY MALCOMIZING

Steel	Case Depth, in. (cm)	Surface Hardness, DPH	Recommended Condition Before Malcomizing
17-4 PH	0.007/0.010 (0.018/0.025)	850/1000	Aged
17-7 PH	0.007/0.010 (0.018/0.025)	850/1000	Aged
PH 15-7Mo	0.007/0.010 (0.018/0.025)	850/1000	Aged
PH 13-8Mo	0.007/0.010 (0.018/0.025)	850/1000	Aged
A-286	0.0035/0.005 (0.0089/0.013)	650/850	Aged
AM-350	0.005/0.007 (0.013/0.018)	950/1000	Solution annealed and refrigerated
AM-355	0.0055/0.008 (0.0140/0.020)	1000/1050	Solution annealed and refrigerated

* A process of the Chapman Valve Company, Indian Orchard, Massachusetts.

Most nitriding furnaces are batch-type units commonly being stationary vertical retort furnaces, bell-type movable furnaces, or box-type movable furnaces. All are equipped with baskets to support the load and have a retort, or the equivalent, which seals the charge so that air and other contaminants are excluded while containing the nitriding atmosphere. An inlet line is provided to introduce the atmosphere, while an outlet line is used to exhaust the spent atmosphere. Appropriate means of heating and temperature control are provided. A fan is usually included in the equipment to circulate the atmosphere and equalize the temperature in the work load [44].

After the depassivated and cleaned work is charged into the furnace, the retort or cover is put in place usually dipping into an oil-filled trough that produces the seal. The air is then purged from the retort in order to avoid production of an explosive gas mixture as well as to prevent the work from oxidizing on being heated. Purging is accomplished with anhydrous ammonia or with nitrogen. The furnace is usually allowed to warm up during purging, say to 300° F (418° K). This facilitates the driving off of moisture. During cooling after nitriding, the ammonia flow is considerably increased. Some furnaces are equipped with a heat exchanger to speed up the cooling process [44].

MECHANICAL TREATMENTS

Treatment of the surfaces of metal parts by mechanical means is designed to accomplish one or more of several purposes, i. e., to (1) improve the finish of the surface of an article, (2) clean, descale, deburr, or put radii on the edges and corners of parts, (3) establish a compressive state of stress at the surface, or (4) cold work the material so as to induce recrystallization in localized areas during subsequent solution annealing. Burnishing and planishing are used to improve surface finish, while explosive hardening, peening, and planishing are used to cold work the metal and/or to develop residual compressive stresses at the surface. Such work and stresses may serve to increase surface hardness, and reduce the occurrence of cracking in welds.

Burnishing

In burnishing, a smooth, glassy, mirrorlike finish is developed on the surfaces of small-to-moderate sized metal parts by frictional contact either

between the parts themselves or between the parts and other pieces of material known in the trade as media. The operation is usually carried out in rotating barrels, shaker containers, or vibrating tubs [49, 50].

In true burnishing, the surfaces of the workpieces are compressed and kneaded, minute high spots being pushed down and other irregularities, such as tiny pits and scratches, being smoothed out and blended by lateral flow of the metal [51]. No abrasion or other form of metal removal takes place. By eliminating superficial irregularities, a high luster is developed. In fact, the process is sometimes called lustering or coloring.

Sometimes the work is polished and burnished at the same time. Because polishing involves metal removal by abrasive action, the operation is often referred to as abrasive burnishing. The degree of metal removal in this operation can be varied from small amounts to almost none. Abrasive burnishing generally does not develop as high a luster as that produced by true burnishing.

Usual practice is to carry out burnishing operations in water, although they can be performed dry. The use of water has several advantages. For example, water tends to act as a cushion reducing the chance that parts will be damaged from battering as they tumble and slide in the container. In addition, water offers lubricating qualities, aids in controlling the fluidity of the mass, and tends to keep dirt away from the metallic surfaces by holding it in suspension. A particularly important function of the water is to act as the solvent and vehicle for additives introduced to increase lubrication, provide cleaning action, control pH, or help to brighten the work.

A high finish can be obtained on stainless steel parts by using stainless steel balls as the burnishing medium [52]. Best practice generally calls for the use of balls of different sizes often mixed with other stainless steel shapes specially designed for the purpose. The sizes and shapes of the pieces comprising the medium are selected with the intention of contacting all the places on the workpiece that require burnishing, without lodging in holes and recesses, or causing the mass to jam together and become rigid [50]. Common nonspherical shapes used in burnishing media are ball-cones, grains, disks, diagonals, ovals, and pins.

Other materials used for burnishing media include leather cuttings, glass beads, corn cobs, hardwood sawdust, and carbon steel or iron balls. Media used for abrasive burnishing include glazed natural stones (such as granite, flint, or agate), shapes made of fused alumina or carborundum, and

glass pellets [50, 52]. When carbon steel or iron balls are used to burnish stainless steel, the operation is followed by a passivation treatment to prevent possible subsequent marring. An effective bath is 10 to 15 percent nitric acid at 140° to 150° F (330° to 336° K) [52]. Although no information relating specifically to the precipitation-hardenable stainless steels has been turned up, there is every reason to suppose that they can be burnished under the same conditions as are applicable to stainless steels in general.

The additives that are introduced by way of the water used in the operation and serve to supplement the action of the medium are known in the trade as compounds. Tallow-base soap is a favored burnishing compound because it produces long-lasting suds that increase luster, provide cleaning action, and act as a cushion [50]. Vienna lime may be added to enhance polishing action; also, the addition of a few ounces of sodium cyanide eggs helps improve the brightness of stainless steel parts [52].

A great variety of burnishing barrels, vibratory machines, and auxiliary equipment is available. Likewise, many different sizes, shapes, and kinds of media are on the market. In addition, a considerable number of compounds of complex chemistry, developed for particular applications, are in use today. Among the last named are wetting agents, water softeners, coloring compounds, cleaning compounds, rust inhibitors, polishing compounds, and chemicals to control the acidity of the water.

In barrel burnishing stainless steel parts, two volumes of the medium are often used to one volume of work, and the barrel is rotated one to four hours depending on the work and the finish desired. The barrel is filled to 50 to 60 percent of capacity, and soap and water are added to nearly cover the work [52]. However, these conditions should not be considered as fixed or standard. Burnishing jobs differ from each other to a greater or lesser extent and the optimum burnishing conditions for each job are generally found by a combination of experience and cut-and-dry methods. To save time and money in setting up burnishing operations it is advisable to consult at some length with the suppliers of equipment and materials. A partial list of suppliers follows:

Equipment Suppliers

Roto-Finish/Ransohoff, Kalamazoo, Michigan
The U. S. Baird Corporation, Stratford, Connecticut
The Pangborn Corporation, Hagerstown, Maryland
Almco Queen Products Division, Albert Lea, Minnesota

The Esbec Corporation, Stanford, Connecticut
Casalbi Company, Jackson, Michigan
Speed-D-Burr Corporation, Los Angeles, California
Rampe Manufacturing Company, Cleveland, Ohio
Hartford Steel Ball Company, Rocky Hill, Connecticut
Chas. F. L'Hommedieu and Sons Company, Chicago, Illinois
Jackson Vibrators, Inc., Ludington, Michigan

Media Suppliers

Norton Company, Worcester, Massachusetts
Almco Queen Products Division, Albert Lea, Minnesota
Roto-Finish/Ransohoff, Kalamazoo, Michigan
The Pangborn Corporation, Hagerstown, Maryland

Suppliers of Compounds

Almco Queen Products Division, Albert Lea, Minnesota
Roto-Finish/Ransohoff, Kalamazoo, Michigan
The Pangborn Corporation, Hagerstown, Maryland

Cleaning, Descaling, Deburring, and Radiusing

The same kind of rotating barrels and vibratory equipment used for burnishing can also be used to perform a number of other surface-treating operations on small-to-medium sized parts. In fact, it is not uncommon to perform two or more operations successively in the same equipment by changing the compound, or the compound and medium, without dumping the work [50]. For example, parts can be successively cleaned, deburred, and burnished in the same barrel if the load is thoroughly rinsed between these operations.

Cleaning can be accomplished by standard immersion or spraying techniques, but it can often be done in a barrel or vibrating tub as a preliminary operation. Stainless steels frequently can be cleaned with combinations of soap, detergents, and mildly alkaline compounds [52].

Barrel tumbling can be used for scale removal as well as for removal of slag remaining from thermal cutting operations. Tumbling media frequently used for stainless steel parts include granite chips, silica sand, aluminum

oxide, and carborundum particles [52]. Grainite chips or fused alumina shapes are frequently used as the medium for deburring and putting radii on edges and corners [52].

Parts made of 17-4 PH and A-286 have been descaled, deburred, and radiused in vibratory equipment using alundum shapes in water [53]. Tubs with capacities of 3, 10, and 70 ft³ (0.0849, 0.283, and 1.981 m³) have been used, the 70 ft³ (1.981 m³) tub being capable of handling 4000 lb (1814 kg) of work pieces per charge. In one trial with the large machine, the load consisted of four six-cylinder marine engine blocks. However, the more common work pieces are small to medium sized machined forgings, castings, screw machined parts, and stampings. To insure complete coverage of the work, the medium is used in a variety of shapes such as diamonds, triangles, and rounds. Desealing, deburring, and radiusing can be carried out in vibrating equipment with no dimensional loss on flat or rounded surfaces. Radii of 0.005 to 0.015 in. (0.0127 to 0.0381 cm) have been obtained, the amount of the radius being subject to close control.

Explosive Hardening

It has been demonstrated that high-intensity shock waves that can be generated by explosives can be used to form a wide variety of metallic components. In fact, in recent years, explosive forming has become a widely used commercial metal forming method. The explosive-forming operation is usually carried out with the metal workpiece at room temperature. Under these circumstances, the effect of the process on mechanical properties is quite similar to that of other cold-forming operations. Thus, metals and alloys that work harden when cold formed will also harden when explosively formed.

It is also possible to harden work-hardenable metals and alloys by the passage of explosive shock waves without deforming the material appreciably. The hardness level reached and the depth of the hardening effect depend on the metallurgical characteristics and the initial properties of the material as well as on the nature of the impulse delivered to the material. The latter factor is subject to considerable control. When hardening rather than forming is the primary objective, the operation is known as explosive hardening as distinguished from explosive forming.

Explosive hardening has not yet achieved any great degree of commercial significance. The major industrial use of explosive hardening thus far has been with Hadfield's manganese steel, which is an austenitic steel containing some 13 percent manganese and 1.25 percent carbon. This type of steel finds extensive use in applications where parts are subject to impacting and heavy abrasion. Examples include railroad frogs, jaws for rock crushers, grinding mill liners, and dipper teeth for power shovels. Such applications involve severe battering and deformation of the parts with the result that they work harden. As a consequence of work hardening during service, the parts become capable of resisting more effectively further deformation and wear as service continues. In many instances, however, the work hardening is only a surface effect and, in most applications, a significant increase in the life of the part could be obtained if it were placed in service already deeply hardened. Conventional methods for deeply hardening this type of steel are expensive and often unsuccessful in realizing the full potential of the material.

However, procedures have been worked out whereby the austenitic manganese steels can be deeply hardened by detonating an explosive charge in contact with the metal. In a favored method of explosive hardening, the explosive is used in the form of thin plastic sheets that are placed in contact with the surface to be hardened. In some cases, only a small area of the component is to be hardened; in other instances, the area may be quite extensive. Again, in some applications, the part is impacted one, two, or even three times to develop the desired hardness and minimize the chance of spalling [54].

Very little research appears to have been carried out on the explosive hardening of the precipitation-hardenable stainless steels, and no industrial usage of explosives as a means of hardening these steels has thus far been identified. However, in one recently completed program on the strengthening of iron-base alloys by means of explosively generated shock waves, A-286 was included among the experimental materials [55]. Using the flying-plate technique, 5- by 5- by 0.25-in. (12.7- by 12.7- by 0.635-cm) specimens of this alloy, as solution annealed at 1800° F (1243° K) for 30 min and oil quenched, were subjected to plane shock waves of 158 and 283 kilobars (1.58 and 2.83 N/m²) pressure.

The effect of shock loading on the hardness of the solution-annealed alloy is shown in Figure 1 [55]. Studies with the electron microscope revealed that shock loading resulted in the generation of large numbers of dislocations and some twinlike bands in the (111) planes of the austenitic matrix. Hardening was ascribed to the presence of this dislocation and twinlike substructure.

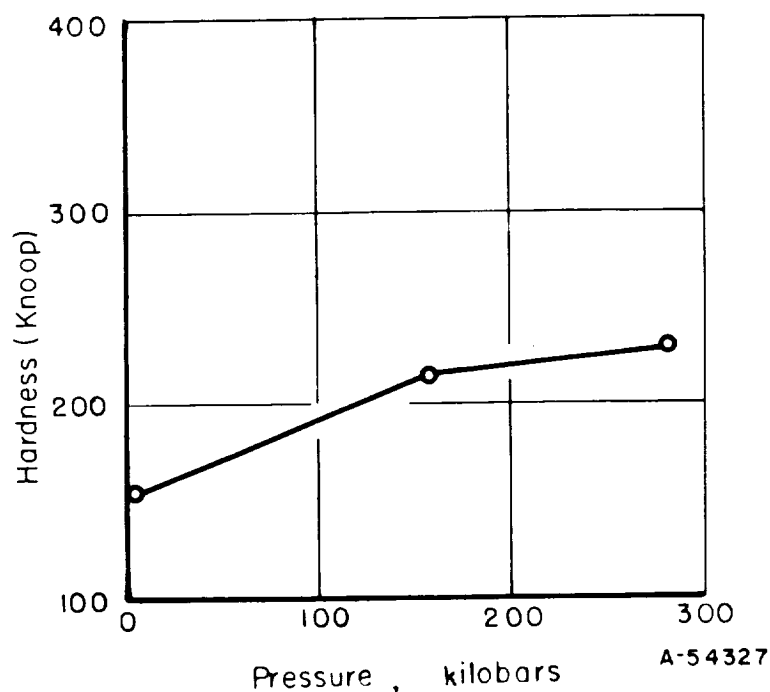


FIGURE 1. EFFECT OF SHOCK LOADING ON THE HARDNESS OF SOLUTION-TREATED A-286 STAINLESS STEEL

Coupons of shocked and unshocked A-286 were aged at 1315° F (976° K) for various time periods ranging from 0.5 to 100 hr. The Rockwell A hardness of the aged coupons was then determined. The results are plotted in Figure 2 [55] as a function of aging time. Knoop hardness numbers obtained by conversion of the Rockwell A values also appear in the figure. Each data point in Figure 2 was reported to represent the average of at least 10 hardness readings.

It is noted from Figure 2 that the shocked materials reached higher hardness values on aging than the unshocked steel and that the maximum hardness was a function of shock pressure. Also, the shocked steels reached maximum hardness sooner than the unshocked material. Again, the percentage increase in hardness was less for the shocked than the unshocked specimens. Electron micrographs of shocked and aged A-286 indicated a homogeneous precipitation of the gamma prime phase. A decrease in dislocation density accompanied aging, most of the remaining dislocations having interacted with precipitate particles. The higher hardness of the shocked and aged alloy was

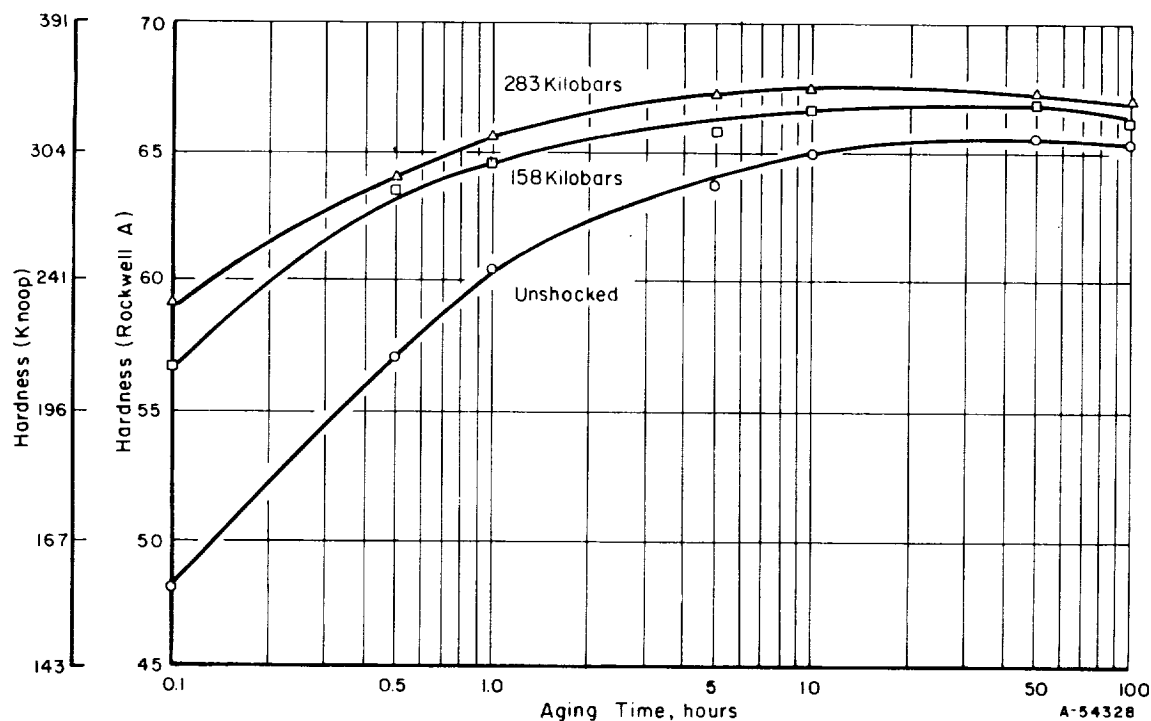


FIGURE 2. AGING RESPONSE OF SOLUTION-TREATED A-286 STAINLESS STEEL IN THE UNSHOCKED AND IN THE SHOCKED CONDITIONS

attributed to the presence of those shock-induced dislocations that had been retained by precipitate-dislocation interaction. The fact that the shocked materials reached maximum hardness faster than the unshocked specimens was thought to be due to faster diffusion rates in the former, brought about by an increase in the density of defects caused by the shock wave.

It would appear that practical applications for the explosive hardening of precipitation-hardenable stainless steels would have to be quite specialized. It is clear that the effectiveness of the shock treatment decreases as the initial hardness of steels in the martensitic condition increases [55]. Thus, explosive hardening probably would contribute no significant amount of additional strength and hardness to fully hardened martensitic or semiaustenitic precipitation-hardenable stainless steels.

On the other hand, shock waves do increase the hardness obtainable with austenitic precipitation-hardenable stainless steels, as can be seen in the results obtained with A-286, and there may be instances where the development

of such an increase in hardness by means of explosives is warranted. However, because explosive hardening resembles work hardening in many ways, the hardness increment due to explosive shocking would probably diminish and finally disappear as the service temperature approached and exceeded the stress-relieving temperature range of the alloy. Again, explosive shocking shortened considerably the time required to reach a given hardness in this alloy on aging. There may be some circumstances under which reducing the aging time by this means effects an economic savings of sufficient size to justify the step.

Planishing

Planishing is the production of a smooth surface finish on metal by a rapid succession of blows delivered by highly polished dies or specially designed polished hammers, or by rolling in a planishing mill [49]. Any readily workable metal or alloy can be planished.

Frequently, planishing equipment is used not only for surface finishing but also for certain metal-forming operations. A common operation applied to sheet metal, which can often be carried out with a planishing hammer, is the process of dishing.

Several types of planishing mills have been developed. One type of roll planishing mill used to planish fusion seam welds, consists of a heavy base that supports a deep-throated superstructure. The superstructure is composed of twin horizontal members at the ends of which the planishing rolls are mounted. The rolls are positioned one above the other and are so mounted that they can be forced together. The upper roll is power driven and serves to drag the work through the rolls, while the lower roll is an idler. Loads up to 50 tons (45 350 kg) can be applied by the rolls [56].

Roll planishing has been found to be a useful mechanical treatment for fusion welds, and especially butt welds. The compressing or upsetting action that takes place in planishing forces protrusions and high spots of weld metal down into the weld. By this process the weld is smoothed and its contour is blended into that of the parent metal. In this way, planishing helps to streamline structures, and improve their aerodynamic characteristics and their appearance. Improvement of contour was an important reason for planishing TIG butt welds in 0.015-in. (0.0381-cm)-thick PH 15-7Mo sheet in connection with the B-70 program [57]. The planishing operation reduced the thickness of the weld approximately 25 percent.

Another application for roll planishing is in producing seam-welded tubular and other components to close tolerances. Here, advantage is taken of the fact that, as the planishing operation reduces the thickness of a weld, it spreads the weld bead laterally at the same time. In the case of a tubular or conical component, for example, the part is made slightly undersized from sheet that has been roll formed and joined by means of a longitudinal butt weld. The weld seam is then run through the planisher one or more times to widen the weld just enough to bring the component up to the desired diameter.

Again, by means of roll planishing, it may be possible to impart sufficient cold work to a weld for it to recrystallize when subsequently heated to an annealing or solution-treating temperature. In this way, the weld takes on the grain structure of a wrought material and becomes more homogeneous. As a result, its mechanical properties tend to more nearly match those of the wrought parent metal than is the case when the weld is not worked. Fusion butt welds made in sheet-metal components formed from PH 15-7Mo have been roll planished so they would recrystallize on subsequent solution annealing [58]. This was done in the production of skin panel assemblies for the B-70. The weld beads were shaved to protrude above the surface of the parent metal some 2 to 4 mils (0.00006 to 0.00012 m) before the planishing operation. After planishing, any excess weld bead was blended with the parent metal by grinding and polishing.

Peening

General Discussion. The term peening originally referred to the cold forming of metals by mechanically working them with hammer blows. It is, in fact, an operation that a metalsmith frequently uses in hand making a metal artifact. However, the smith also knows that by peening in a certain way he can often improve the article's resistance to cracking and breaking especially under conditions of repeated or cyclical loading. To bring about this improvement in performance, he strikes may light, quick blows against the metal that is essentially at room temperature, the blows being too light to produce an appreciable change of shape in the article. Under these conditions the craftsman in working only the surface of the metal [59].

Today, peening is more often thought of as a means of mechanically working the surface of a metal than as a procedure for metal forming. The operation is accomplished by hammer blows or by the impingement of shot.

Carried out in this manner, peening causes a limited amount of plastic flow in the surface of the work, tending to increase surface area; however, this action is resisted and restrained by the unworked interior. As a result of the restraint, compressive stresses tend to build up in the peened surface layers of the article, while counterbalancing tensile stresses tend to develop in the interior [60, 61]. It is largely the capability of peening to develop residual compressive stresses at the surface of a metal that makes it a useful metallurgical operation. Residual stresses can be built up in any metal that strain hardens.

Hammer peening is carried out manually by means of hand hammers or mechanically with pneumatic and other power hammers or with equipment, such as swaging machinery, that acts in a similar manner [62]. Mechanical hammer peening is often not convenient to apply; manual hammer peening is more adaptable and usually cheaper. However, hammer peening in general is difficult to control. Shot peening is much more amenable to control; it is a flexible operation and is quite widely used in a variety of applications.

Shot peening is usually done in a cabinet to confine the shot, contain dust, and aid in the recovery of the shot for reuse. The work to be peened is introduced and supported mechanically. Various materials are used for shot; cast iron and steel shot are generally used topeen workpieces made of steel. For stainless steel and nonferrous work in which contamination of the surface with iron from the shot is unacceptable, other materials usually are used; shot composed of glass beads or cut stainless steel wire is a frequent choice. Cast iron grit, sand, and other abrasive materials are not used because they abrade and roughen the surface of the work. Usual shot sizes range from 0.0156 to 0.09 in. (0.04 to 0.23 cm) in diameter. The shot may be driven against the work by an air blast or by the centrifugal force generated by a rapidly rotating, radially vaned wheel into whose hub region the shot is fed for distribution to the work by means of the vanes.

The important factors in shot peening are the magnitude of the compressive stresses developed in the surface layers of the metal, the depth of the effect, and the coverage or uniformity with which the peening operation is carried out over the surface of the metal. Stress and depth are strongly influenced by the characteristics of the material being peened. In addition, stress, depth, and coverage are influenced by such variables as the velocity, size, hardness, and shape of the shot; the amount of shot striking the work; the shape and size of the area covered by the shot stream; and the angle with which the shot impinges on the work. These variables are subject to control.

Optimum conditions and settings for any given application are determined by experimentation. Further information on shot-peening procedures is given in the literature [59, 60, 61].

Applications for which peening has been used include the following:

1. Improvement of fatigue strength (although it is not beneficial under conditions of very high-stress, low-cycle fatigue [63]. The residual compressive stresses built up at the surface are considered largely responsible for the beneficial effect of peening on fatigue properties. This is the major application for shot peening.

2. Correction of distortion in weldments and in unwelded components. In some cases, this may be brought about through considerable plastic flow of the metal; more commonly, distortion is corrected by the change in the internal stress state of the metal produced by the peening operation.

3. Prevention of cracking in weldments. The objective is to counteract the tensile stresses developed in the joint by the shrinkage that occurs on cooling after welding.

4. Straightening components. Again, this may be done by plastically deforming the metal (especially cold forming) or by altering the internal-stress state of the component.

5. Improvement in resistance to stress-corrosion cracking. The objective is to overcome the surface tensile stresses necessary for stress-corrosion cracking by introducing compressive stresses through the peening operation. For this kind of application, shot peening is the method usually employed.

6. Closing up of porosity in castings and weldments.

7. Forming of parts. Shot peening is quite well adapted to mild bending and contouring operations on large expanses of relatively thin gage material. The changes in curvature result from the action of the internal stress system produced by the peening.

8. Promotion of recrystallization. It is often possible to introduce enough cold work into welds and weld-heat-affected zones, as well as into

wrought components, by peening to cause the metal to recrystallize when subsequently heated to an annealing temperature. Recrystallization of welds may result in improved ductility and toughness.

Precipitation-Hardenable Stainless Steels. References relating specifically to the peening of precipitation-hardenable stainless steels are quite infrequent. However, these alloys can be strain hardened and, therefore, can be expected to respond to peening operations.

An example of the effect that peening can have on fatigue resistance is the improvement in resistance to tension-tension fatigue produced in spot-welded joints on A-286 by peening the welds [64]. The joints were made in 0.050-in. (0.127-cm)-thick sheet that had been solution annealed 10 min at 1800° F (1243° K), oil quenched, and aged 16 hr at 1325° F (982° K). Figure 3 shows S-N curves obtained for a 4-spotweld lap joint of the material when tested as welded and as peened with a flat-ended punch [64]. It is evident that an impressive increase in fatigue strength resulted from the peening operation.

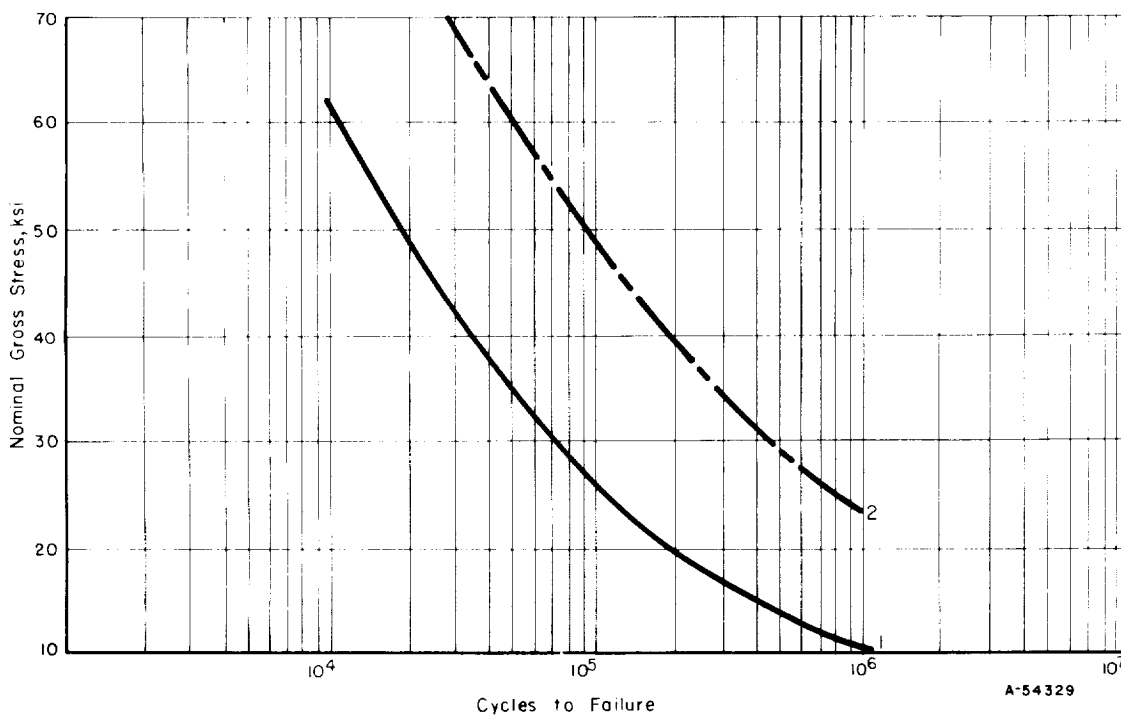


FIGURE 3. FATIGUE-TEST RESULTS FOR A 4-SPOTWELD LAP JOINT MADE IN 0.127-cm THICK AGED A-286 SHEET

It is doubtful that there would be much call for peening to correct distortion in weldments or to straighten parts made of precipitation-hardenable stainless steels, because full heat treatment frequently follows fabrication of articles from these steels, and this step affords a good opportunity for sizing and straightening. On the other hand, there might often be merit in heavily peening welds made in these steels prior to full heat treatment. During the solution treating step, heavily worked welds would have a chance to recrystallize with concomitant improvement in ductility and toughness.

CONCLUSIONS AND RECOMMENDATIONS

The precipitation-hardenable stainless steels offer numerous combinations of desirable properties which fit them to serve successfully in a wide variety of important applications. As a consequence, it is seldom necessary to augment or supplement their capabilities by special surface treatments, whether of the coating or the mechanical type.

In some cases, certain surface treatments are, or can be, used to advantage with these steels. Notably, their wear resistance can be improved by hard surfacing; their resistance to stress-corrosion cracking may be increased by electroplating or electroless plating; and their surface hardness, wear resistance, galling resistance, and fatigue strength can be improved by nitriding. Planishing is effective in contouring welded joints in these steels, while peening is a useful method of improving their fatigue resistance. Carburizing, decarburizing, and scaling during high-temperature heat treatment can be inhibited or prevented by the application of protective coatings to the surface prior to the heat treating operation.

The cracking of the coating that occurs in the process of hard surfacing the martensitic precipitation-hardenable stainless steels is a problem in that it limits the range of usefulness of the hard-surfaced material. Service conditions must feature wear principally, and may be no more than mildly corrosive. If a coating could be developed that would provide a high degree of wear resistance but would not crack on cooling from the fusion temperature, when applied to the martensitic type of steel, then the variety of applications for this material should increase substantially. In particular, the material could be used in applications requiring the combination of high strength corrosion resistance, and wear resistance, which is not an uncommon set of requirements. The

coating would need to possess sufficient ductility to allow it to adjust to the expansion that occurs in the base metal as it undergoes the austenite-to-martensite transformation on cooling from the fusion temperature to room temperature.

Another problem is presented by the coatings currently used to protect the precipitation-hardenable stainless steels from scaling and decarburizing during high-temperature heat treatment. Most of these coatings perform their protective function acceptably. However, all of them are difficult to remove after heat treatment. It is common practice to condition them in an alkaline salt bath at an elevated temperature, such as 900° F, and then flash pickle in a nitric acid-hydrofluoric acid solution. These steps are expensive. In addition, there is danger that the acid pickle may damage the metal. It would be highly desirable to develop protective coatings that are easier to remove after heat treating. Water-soluble coatings would be preferred, but coatings that could be removed by water or steam jets would be acceptable.

It is recommended that consideration be given to further research on the two problems described above.

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APPROVAL

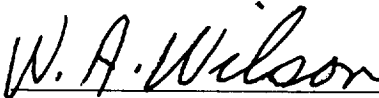
April 27, 1967

SURFACE TREATMENTS FOR PRECIPITATION -
HARDENING STAINLESS STEELS

By A. M. Hall

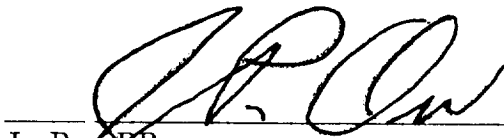
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This document has also been reviewed and approved for technical accuracy.



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